CC=EP DATE=19891206 KIND=A2 PN=0344430

METHOD FOR PRODUCING A PLASTER OF PARIS SUITABLE FOR THE PRODUCTION OF GYPSUM PLASTERBOARDS FROM FGD GYPSUM (VERFAHREN ZUR HERSTELLUNG EINES FÜR DIE PRODUKTION VON GIPSKARTONPLATTEN GEEIGNETEN STUCKGIPSES AUS REA-GIPS)

DR. HEINZ RENNEN, ET AL.

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. FEBRUARY 2011
TRANSLATED BY: SCHREIBER TRANSLATIONS, INC.

PUBLICATION COUNTRY	(10):	EP
DOCUMENT NUMBER	(11):	0344430
DOCUMENT KIND	(12):	A2
PUBLICATION DATE	(43):	19891206
APPLICATION NUMBER	(21):	89106119.4
APPLICATION DATE	(22):	19890407
INTERNATIONAL CLASSIFICATION	(51):	C04B 11/26, C04B 28/14, //(C04B28/14,22:11,24:12)
PRIORITY COUNTRY	(33):	DE
PRIORITY NUMBER	(31):	3818992
PRIORITY DATE	(32):	19880603
INVENTOR(S)	(72):	DR. HEINZ RENNEN, ET AL.
APPLICANT(S)	(71):	RIGIPS GMBH RÜHLER STRASSE
DESIGNATED CONTRACTING STATES	(84):	AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, LU, NL, SE
TITLE	(54):	METHOD FOR PRODUCING A PLASTER OF PARIS SUITABLE FOR THE PRODUCTION OF GYPSUM PLASTERBOARDS FROM FGD GYPSUM

FOREIGN TITLE [54A]: VERFAHREN ZUR HERSTELLUNG
EINES FÜR DIE PRODUKTION
VON GIPSKARTONPLATTEN
GEEIGNETEN STUCKGIPSES AUS
RBA-GIPS

Method for Producing a Plaster of Paris Suitable for the Production of Gypsum Plasterboards from FGD Gypsum

Gypsum plasterboard is a structural material that has the greatest popularity and use worldwide and has experienced dynamic development around the world in recent decades.

Thus, for example, 6 m 2 of gypsum plasterboard per capita of the population was produced in 1978 in the USA. Gypsum plasterboard is also in universal use and is regulated by various standards in the Federal Republic of Germany.

Gypsum plasterboard is manufactured by a continuous method on large conveyor belt systems. The most important parts of the production line are:

- Bottom paperboard infeed that forms the visible face of the board,
- Plaster of Paris paste infeed and distribution by calibrated rollers with simultaneous top paperboard infeed that forms the back of the board,
- Setting section with cutters in the form of shears,
- Turning bench with input into the multi-stage dryer, and
- Delivery and board bundling.

The setting process of the gypsum plasterboards and the length and conveyor speed of the setting section are matched to

one another. Modern production lines with high conveyor speeds can comprise setting sections up to 300 m long. Both plaster of Paris from natural gypsum deposits and chemical gypsum, synthetic crude gypsum that occurs, for example, in wet phosphoric acid production, can be used as raw material. The gypsum plasterboard manufactured on the conveyor belt consists of a gypsum core rolled out wide that is jacketed with paperboard including the long edges, while the crosscut edges show the gypsum core. The paperboard is tightly joined to the gypsum core. The gypsum core may contain suitable aggregates or additives, and may be aerated. The endless gypsum plasterboard manufactured on the conveyor belt is flat and is cut at right angles into generally long lengths between 200 and 450 cm. It is 125 cm wide and between 9.5 and 25 mm thick. The structural

Gypsum plasterboards are differentiated according to their manufacture and the use for which they are intended, depending on their nature.

Differentiation is therefore made between gypsum structural plasterboards, gypsum fire protection plasterboards, girder plaster tiles, and impregnated gypsum plasterboards. The latter are again differentiated into impregnated gypsum structural plasterboards and impregnated gypsum fire protection plasterboards.

There are also coated gypsum plasterboards with solid coatings, films, or made of plastic compositions. The coating is governed by the intended application, such as films of plastic or aluminum as vapor barriers, films of plastic for decorative purposes, films of rolled lead to attenuate X-rays, copper sheets for decor, and plastic compositions with or without fabric inserts to improve surface hardness or for decorative surface structures.

Then there are gypsum plasterboards that are bonded on the back with insulating materials and are called composite boards. Finally there are panels of gypsum plasterboard that are provided with different holes and slots and are used as decorative sound-absorbing wall and ceiling paneling. The configuration of the edges of gypsum plasterboard is particularly important. There are different edge forms:

- Flattened Edges,
- Full Edges,
- Round Edges,
- Angled Edges,
- Round Flattened Edges, and
- Wedge-Shaped Edges.

The dynamic dissemination of gypsum plasterboards is taking place essentially because of the properties of the gypsum plasterboard. These originate specifically from the combined

effect of the gypsum core and the paperboard jacketing. The paperboard acts as a tensile reinforcement and gives the boards the necessary stiffness. Because of this, substantial spans can be bridged by gypsum plasterboards in spite of their small thickness. On the other hand, the boards are light. They can be easily transported, handled, and processed. Their flexural softness is an important prerequisite for the design of sound-absorbing structural components.

The board surface in turn is a very good substrate for paints and coatings, especially for bonding to wallpaper, tiles, and other coverings.

/2

The board coating is very important for the quality of the board. The different properties of the board that are direction-dependent also depend on it. Thus, strength and elasticity in the direction of the paperboard fibers, i.e. in the longitudinal direction of the boards, are greater than those that are perpendicular to the direction of the paperboard fibers. This has to be considered in practical processing, since for example the greater flexural strength and the greater deformation resistance can be utilized beneficially by the longitudinal mounting of the boards.

The gypsum plasterboard also has advantageous properties in the aerated state, because it is able to absorb moisture and

quickly release it again, which is not the case with concrete, for example (Hanusch, "Gypsum Plasterboards", Drywall Construction, Assembly Construction, Expansion, 1978).

In the course of the increasing return of mankind to natural ways of life, and thus to a clean environment in which neither land nor water nor air is contaminated with pollutants, there is more and more change to cleaning the flue gases from large combustion plants, especially from power plants, i.e. after separating out the dusts contained in the flue gases, which has already been done, harmful chemical compounds are now also to be removed, namely sulfur dioxide (SO₂).

During the separation of sulfur dioxide, gypsum (calcium sulfate dihydrate) is formed, which in turn is utilized by the gypsum-processing industry, all the more so since natural gypsum deposits are lacking, are available only in limited amounts, or possibly should not be mined for reasons of nature preservation. The gypsum-processing industry has therefore been concerned from an early time with this gypsum occurring as flue gas desulfurization gypsum.

Thus, for example, it is known how to process this flue gas desulfurization gypsum, called FGD gypsum below, into various hemihydrates and how to use them instead of natural gypsum (Ullmann, 4th Ed. 1976, Vol. 12, p. 302).

US-PS 4 502 901 discloses how to process FGD gypsum to manufacture plasterboards. To do this, FGD gypsum obtained with 10 to 15% free moisture is dried in a flash dryer to 0 water content, then calcined to remove 75% of the water of crystallization, and finally ground to twice its surface area.

The production of gypsum plasterboards is said to be successful with gypsum produced in this way.

The gypsums formed in the flue gas desulfurization system, however, have a number of undesirable properties that make it difficult to process them directly, even when the FGD gypsum is first dried to 0 moisture, calcined, and ground. From their history of formation, FGD gypsums have such good flow characteristics because of their very narrow particle size range in their powdered form that unwanted difficulties arise in the elevators used for transporting them. Suspensions of unground FGD gypsum and water show decidedly viscous behavior when stirred. They show pronounced thixotropy and poor flow properties, and they have a very much higher water demand than natural gypsum.

The last point in particular is extremely detrimental for producing gypsum plasterboards in well-known continuous processes under economical conditions.

The task underlying the present invention, therefore, is to propose a method by which a product equivalent to natural gypsum

can be made from FGD gypsum and that is suitable for producing gypsum plasterboards of a wide variety of types and for a wide variety of purposes and applications.

This task is accomplished pursuant to the invention by continuously calcining the dried FGD gypsum in a cooker equipped with a conical firing chamber, then grinding the calcined product in a mill with high energy impact, and pre-wetting the ground product with amounts of water between 1 and 8 wt. % for 1 to 3 minutes before mixing the gypsum.

The calcining of the dried FGD gypsum in a conical cooker through which the calcined product is moved continuously and thereby forms a quasi-fluidized bed, provides a very homogeneous uniform calcined product with excellent efficiency of the order of magnitude of 82%.

The grinding process following the calcining is to take place with high energy impact, preferably in a ball mill. This improves the flow properties of the slurry mixed with water and thus improves the crystal habit, and in turn a smaller water demand is achieved despite the larger surface area. It was found that grinding in an ironclad tube mill equipped with steel balls with a diameter of 20 to 25 mm, preferably 22 mm, and so-called hammer balls with a diameter of about 80 mm for constant cleaning of the small balls that tend to become coated, gives the product especially good and advantageous processing

properties. The speed of rotation of the mill is set accordingly for the customary technique.

/3

The following treatment of the dried and ground gypsum, done with a small amount of water of 1 to 8 wt.%, preferably 5 wt.% water, and with a residence time of 1 to 3 minutes to anneal the surface, before it is fed in to the gypsum mixer, improves the consistency of the product.

The slurry produced in the gypsum mixer is then processed further in a known manner. Extenders or other additives may be added to the slurry in a known manner.

If desired or available, a vibrating tube mill can be used instead of the ball mill. It is important for the mill to achieve high energy impact and activation of the hemihydrate produced from FGD gypsum.

On the other hand, the FGD gypsum ground by agglomerating grinding in the ball mill or vibrating tube mill shows a lower water demand in mechanical mixing, a specific surface area that corresponds to the product originating from natural gypsum, better mixing properties, and no longer has thixotropic properties.

The FGD gypsum from agglomerating grinding with the ball mall or vibrating tube mill according to DIN 11 68 has a water-gypsum factor (WGF) of 0.66 with a Blaine surface area (cm^2/g) of

4,700, and after particle breakup by mechanical mixing it has a Blaine surface area (cm^2/g) of 12,000. The bulk weight of the plaster of Paris is 900 q/l.

The treatment of the product pursuant to the invention in the last process step, preferably with 5 wt. % water, represents artificial aging that is known per se. It reduces the mixing water requirement. This is preferably done in spray mixer systems with mechanical stress on the bulk product, in which the gypsum particles are separated by severe turbulence and partial fluidization.

The large surface area produced in this way with simultaneous water jet treatment provides uniform wetting of each individual grain.

The delicate problem of the pre-wetting of plaster of Paris can be carried out on an industrial scale with such mixers and means a substantial reduction of the need for drying energy for the gypsum plasterboards produced.

Mixers of this type are made by the Schlugl Company, for example.

A flue gas desulfurization gypsum pre-wet and artificially aged by the method described, with flow properties equivalent to those of the gypsum-water suspension, has a substantially smaller water demand. The achievable water saving amounts to as

much as 25-30%. This means a considerable reduction in drying energy, which likewise is of the order of magnitude of 25-30%.

It has been found that with an FGD gypsum treated in the manner described above, gypsum plasterboards can be produced that correspond to those made from natural gypsum, and it is especially beneficial that this treated FGD gypsum can be used for gypsum plasterboards that have a low specific gravity.

Comparative tests are shown side by side in the table below, between gypsum plasterboards with a thickness of 12.5 mm produced on the one hand by the method pursuant to the invention and using FGD gypsum as starting material, and using natural gypsum that was calcined in a rotary kiln.

		RE/	Naturgips Orehofen 12,5		
Plattendichte	mm	12,5			
Flächengewicht	kg/m²	12,5	11,3	9,0	11,2
Bruchlast	N				
längs		690	719	700	675
quer		310	270	250	250
Biegezugfestigkeit	N/mm²				
längs		8,2	8.5	8,4	8,1
quer		3,8	3,2	3,0	3,0
Verformung	mm			***************************************	
längs		0,40	0,44	89.0	0,45
quer		0,43	0,57	0,74	0,55
E-Modul	N/mm²		1		
längs		5000	4500	2900	4400
cnet		4700	3500	2700	3600
Druckfestigkeit	N/mm²	10.2	9,0	4,0	9.0
Kugeldruckhärte	N/mm²	18,3	17,4	6,1	17,0
Kartonhaftung	%	100	100	100	100

		Ground FGD Gypsum			Natural Gypsum Rotary
					Kiln
Board thickness	mm	12.5			12.5
Basis weight	kg/m ²	12.5	11.3	9.0	11.2
Breaking load					
Lengthwise					
Across					
Flexural					
strength					
Lengthwise	[See	original Ge	rman for da	ita]	
Across					
Deformation					
Lengthwise					
Across					
Modulus of					
Elasticity					
Lengthwise					
Across					
Compressive					
strength					
Ball indentation					
hardness					
Paperboard					
adhesion					

With selective establishment of the setting time of the FGD gypsum/water suspension by simultaneous use of setting accelerators and retarders, it is possible to add to the suspension up to 20% FGD dihydrate and inert fillers such as powdered limestone, fly ash, or vermiculite, without changing the setting properties of the mixed gypsum.

FGD dihydrate activated in ball mills in the order of magnitude of up to 2% based on the calcined gypsum is used as the preferred accelerator. Salts of polyoxymethylene amino acid are used advantageously as retarders.

Formula for Gypsum Plasterboards Made from FGD Gypsum needed for producing 1 m^2 of 9.5 mm thick boards are:

6.7 kg	FGD gypsum, calcined
4.3 kg	Mixing water
0.025 kg	Acid-modified cornstarch or wheat starch
0.002 kg	Nonionogenic and anionic surfactants
0.100 kg	Ball mill activated FGD dihydrate accelerator
0.001 kg	Polyoxymethylene amino acid (Ca salt)
0.400 kg	Paperboard, 0.3 mm thick

A portion of the FGD gypsum can be replaced by a proportion of up to 20% of "brack" that is ground to a characteristic particle size. "Brack" here is waste from gypsum plasterboard production, or fragments of board, in which the proportion of paper may be reduced by screening and sifting. Brack is therefore breakage from gypsum plasterboards that occurs during production or handling and is ground to a suitable particle size. The binder fraction can contain additionally up to 20% natural gypsum (dihydrate) and up to 20% anhydrite.

To pursue the concept of the invention, the calcined product is ground with high energy impact in the mill to a Blaine surface area of $2,000 - 6,500 \text{ cm/g}^3$ [sic], but preferably to a Blaine surface area of $3,000 - 5,000 \text{ cm}^2/q$.

/5

Claims

 Method for producing a plaster of Paris from FGD gypsum that is suitable for the production of gypsum plasterboards, by drying the FGD gypsum, calcining to the hemihydrate, and grinding to a larger surface area, characterized in that the dried FGD gypsum is calcined continuously in a cooker equipped with a conical firing chamber, the calcined product is then ground in a mill with high energy impact, and the ground product is wet with amounts of water between 1 and 8 wt.% for 1 to 3 minutes before mixing the gypsum.

- Method pursuant to Claim 1, characterized in that the calcined FGD gypsum is ground in a ball mill or in a vibrating tube mill.
- 3. Method pursuant to Claim 1 and 2, characterized in that the dried and ground hemihydrate is pre-wet with small amounts of 1 to 8 wt. % water and that a residence time of 1 to 3 minutes is observed before further processing.
- Method pursuant to Claim 3, characterized in that the added amount of water is preferably 5 wt. %.
- 5. Method pursuant to Claim 1 to 4, characterized in that a fraction of up to 20 wt. % FGD dihydrate is added to the plaster of Paris.
- Method pursuant to Claim 1 to 5, characterized in that inert fillers such as powdered limestone, fly ash, and vermiculite are added.
- 7. Method pursuant to Claim 1 to 6, characterized in that FGD dihydrate activated in ball mills is added to the plaster of Paris as an accelerator in an amount of up to 2 wt. % based on

the calcined gypsum, and salts of polyoxymethylene amino acid are added as retarders.

- 8. Method pursuant to Claim 1 to 4, characterized in that the grinding process following the calcining is carried out in a ball mill with steel balls 20 to 25 mm in diameter, preferably 22 mm, and hammer balls 80 mm in diameter.
- 9. Method pursuant to Claim 1 to 8, characterized in that the calcined product is ground in a mill with high energy impact to a surface area of 2,000 6,500 cm 2 /g, preferably to 3,000 5,000 cm 2 /g.